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1.1 Introduction

In 2007, a continuation of experiments studying the uptake kinetics of a DPB getter material was conducted [1,2]. In these experiments, a powder formed from ground pellets of DPB getter as currently deployed was subject to multiple hydrogenations in an isopiestic hydrogen reactor. The objective was to observe the reaction kinetics of the powdered material as a function of ambient hydrogen pressure at room temperature, with the intention of resolving key issues of the DPB reaction mechanism that could relate to its aging and capacity characteristics. The results indicated, in agreement with work performed in 2006 as part of the same project, that the likely mechanism of DPB/Hydrogen reaction occurs via the diffusion of unreacted DPB toward the catalyst surface. They also demonstrated that at a sufficiently high pressure (on the order of a few torr) of hydrogen, the reaction was vigorous enough to release sufficient heat to vaporize both the DPB getter and its hydrogenate away from the surface of the Pd catalyst at which the reaction takes place. The consequence was a premature slowing of the reaction kinetics and a drop in overall capacity.

In the present work, the isopiestic reaction scheme is expanded to study the dependence of the reaction rate of this material on both hydrogen pressure and temperature. The dependence of the reaction rate on both temperature and pressure can provide both valuable clues about the reaction mechanism, as well as the activation energy of the principal reaction. The activation energy is an especially important term for purposes of doing lifetime predictions for getters under conditions of varying temperature.

1.2 Method

The isopiestic hydrogen reactor used in this set of experiments is the same as described previously. Temperature control was achieved by wrapping the main chamber in a blanket heater driven by an autotransformer. Temperature was measured at the sample with a steel jacketed type K thermocouple welded into a through-hole in the chamber wall. Temperature was calibrated by the voltage setting on the transformer, and was varied from room temperature to 75 °C. Hydrogen pressure was varied from 1 Torr to 8 Torr. Owing to the appreciable vapor pressure of DPB and its hydrogenates above room temperature, two different reaction schemes were carried out. In the first, the sample was heated to temperature under dynamic vacuum, then further evacuated for approximately 12 hours. This better guaranteed a near zero starting pressure at the expense of losing some DPB to sublimation. In the second type of experiment, the sample was evacuated overnight at room temperature, and was then heated after isolating the main chamber from the vacuum service. By evacuating only at room temperature, DPB losses were minimized. However, heating under static vacuum allowed the material to build up a

measurable vapor pressure capable of skewing the target pressure of the flow controller. Therefore, this pressure, which varied from a fraction of a Torr to well over 2 Torr was added to the pressure setpoint as an offset.

1.3 Results and Discussion

Figures 1 and 2 present the net (integrated) kinetics as hydrogenation pressure as a function of time. Clearly, the experiments of type 2 present highly anomalous behavior, showing what appears to be a completely inverted temperature response of the reaction kinetics. In contrast, the type 1 experiments are much better behaved. On the basis of this behavior, the type 1 experimental data were fully analyzed for activation energies, despite the expected loss of some DPB during the pumping stages, especially at the

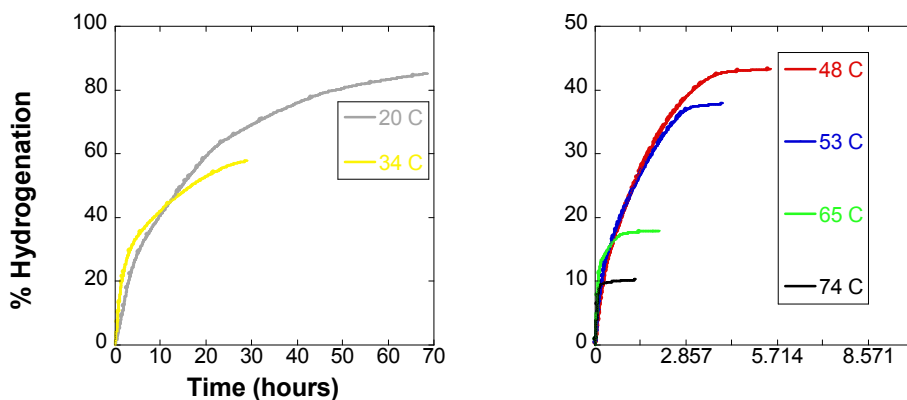


Figure 2. Data from experiments of type 1

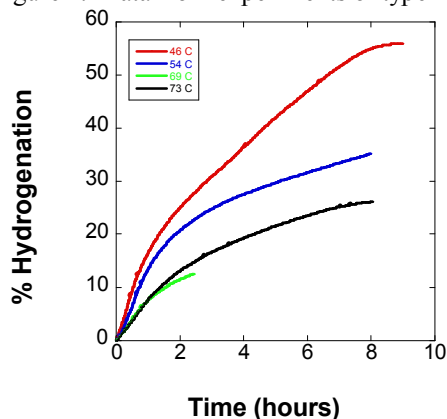


Figure 1. Data from experiments of type 2

higher temperatures.

In order to evaluate the activation energy with maximum accuracy, it would be necessary to either correct the net reaction rate by knowing the mass loss of material during heating

(cf. reference 3), or by knowing the vapor pressures of the different species formed during the reaction cycle. The experiment as performed did not have the capability to do mass measurements. While the reaction speciation is likely to be complicated, a current collaboration with the United Kingdom's Ministry of Defence seeks to measure the vapor pressures of a range of DPB hydrogenates of hydrogen stoichiometries from 1 to 8. This data can be subsequently applied to improve the estimates of activation energy. However, it will not be available until late 2009.

For the moment, the activation energy is best estimated on the basis of the initial kinetics. Given the work from the last two years, our current understanding of the mechanism of this material is that as DPB is consumed, fresh DPB must diffuse to the surface of the Pd to react with H and sustain any further reaction. An unreacted, unheated sample of the getter is 75% by mass DPB. After heating, some amount of the fresh DPB will be lost from the sample. Provided a substantial proportion is left behind, the initial reaction rate with respect to the DPB activity will remain unchanged, since the DPB is still a bulk phase in contact with the Pd catalyst (i.e., the DPB activity is defined as 1). Thus, a measure of the early reaction rate will give an accurate reflection of the impact of temperature on rate, irrespective of limited losses of DPB material to sublimation.

Linear extrapolations were made of the early parts of the data sets of figure 1 to represent the initial kinetic rate. These values were plotted in standard Arrhenius fashion as shown in figure 3, and a corresponding first-order activation energy was derived, equal to

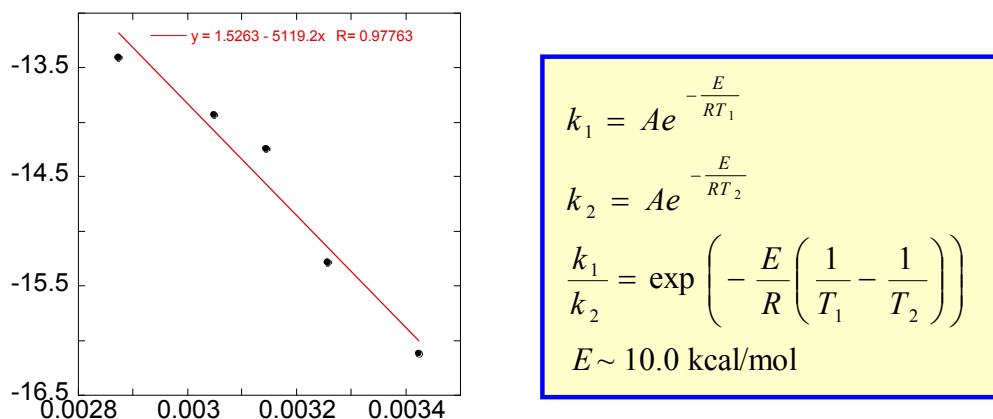
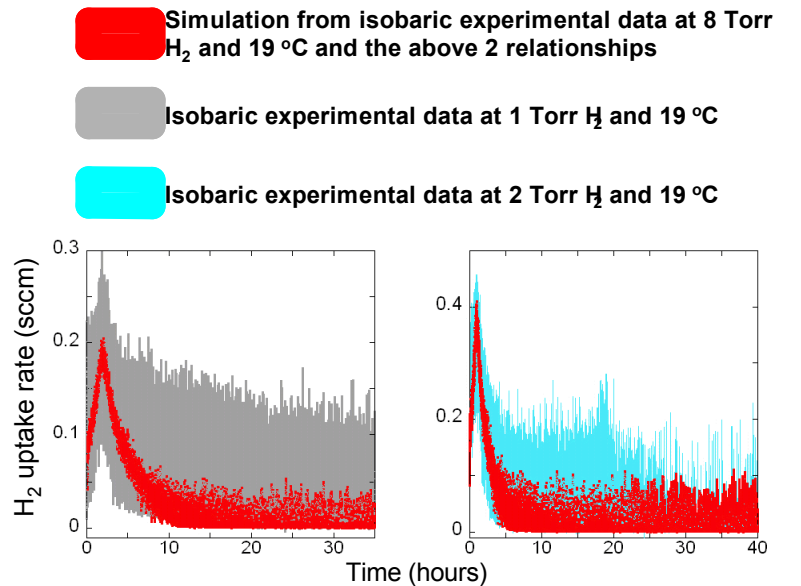


Figure 3. Arrhenius estimate of the activation energy of ground DPB getter hydrogenation

approximately 10 kcal/mol. The consistent increase in initial rate with temperature and the resulting well-behaved log-linear behavior of the data justify the assumption that after heating an amount of DPB adequate to provide accurate kinetic data remained.

In other work that examined the kinetic behavior of the hydrogenation of pressed pellets of DPB getter, it was established that the reaction was limited with respect to hydrogen diffusion into the pellet [3]. Assuming that the diffusion coefficient is independent of either pressure or activity of hydrogen dissolved in the solid, it was shown that $P_1 t_1 = P_2 t_2$, where P is pressure and t is time. This further implies that $\text{rate}_1 = (P_1/P_2)(\text{rate}_2)$. It is reasonable to assume that there is likewise a similar barrier to gas diffusion into the granules of ground getter material used in the present work. On this basis, the anticipated instantaneous rates at 19 °C and 1 and 2 Torr were predicted from the instantaneous rates at 19 °C and 8 Torr, figure 4. The synthetic data agrees reasonably well with the actual data measured at 2 Torr, but rather underpredicts the actual response measured at 1 Torr. Put another way, the rate at 1 Torr is higher than would be expected from the rate measured at 8 Torr, provided the equations above hold true. It is possible there is an irregular diffusional behavior of hydrogen dissolved in the getter material as a function of its ambient pressure. However, the experiments reported in 2006 and 2007 suggest that the rate of reaction of the DPB system is modulated by the heat generated by the hydrogenation reaction, such that a relatively high pressure can induce sufficient heat to vaporize organic material from the near catalyst region, thus resulting in impeded diffusion of fresh getter to the catalyst surface. Prior to this event, however, the added heat would serve to speed the initial reaction by accelerating getter diffusion. It is this



effect that is the likely cause of the overprediction of the rate at 1 Torr, as shown in figure 4.

1.4 Conclusion

We have isolated the activation energy of DPB hydrogenation in the DPB getter system. We intend to incorporate this important value into more complete predictions of getter lifetime that account for changes in the temperature profile of the sample. We have also

developed further substantiation of the model presented previously of reaction heat and getter diffusion as kinetic factors in the DPB system.

1.5 References

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